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Electrochemical fluorosulfation of perfluoroallylbenzene

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Abstract

Perfluoroallylbenzene (**I**) can be isomerized under the action of HSO_3F to form perfluoropropenylbenzene (in the form of a mixture of *cis*- and *trans*-isomers) which undergoes anodic oxidation in HSO_3F to give α,β-bis(fluorosulfonyloxy)perfluoropropylbenzene (**III**). Reaction of **III** with CsF in tetraglyme gives perfluoro-2-methylbenzoxolene (**XII**), whereas **III** is converted to perfluoromethylphenyl-α-dione (**IX**) by reacting with AcONa/AcOH. Cyclization of (**IX**) catalyzed by CsF occurs to form perfluoro-2-methyl-3-oxobenzoxolene (**XIII**).
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1. Introduction

Recent studies have shown that fluorinated α-alanine derivatives synthesized from pyruvic acid exhibit various physiological activities and can be used for the syntheses of pharmaceuticals [1]. In this connection, it seemed interesting to develop a method for the synthesis of perfluorobenzylglycolic acid, which is the possible precursor for a second fluorinated amino acid, α-hydroperfluorophenylalanine.

Vicinal aliphatic bisfluorosulfates can be considered as latent α-dicarbonyl compounds [2]. In their turn, α,β-bis-(fluorosulfonyloxy)perfluoroalkanes are formed easily from perfluoroalkanes either by reaction with peroxydisulfuryl difluoride [3,4] or by electrochemical fluorosulfation under conditions of anodic oxidation of perfluoroalkenes [5,6] or fluorosulfonic acid [7,8].

Thus, we could expect that anodic oxidation of perfluoroallylbenzene (**I**) in HSO_3F would give β,γ-bis(fluorosulfonyloxy)perfluoropropylbenzene (**II**) whose hydrolysis would make it possible to obtain perfluorobenzylglycolic acid.
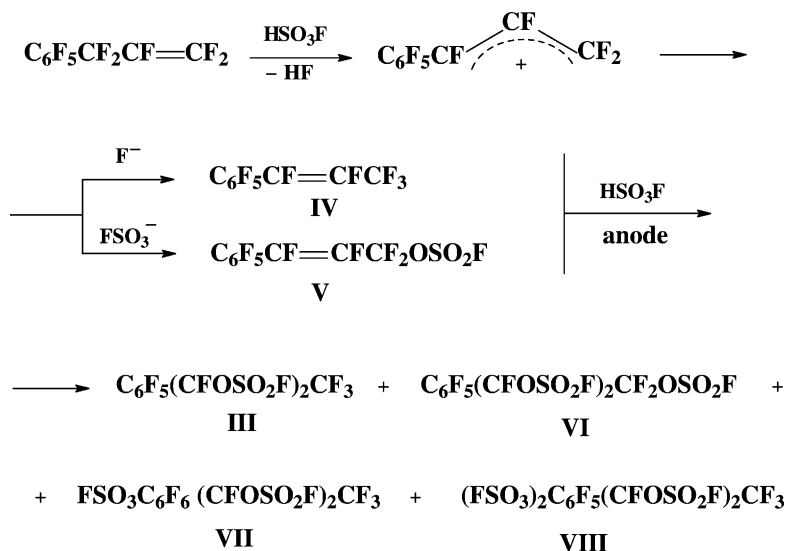
2. Results and discussion

Unexpectedly, for the electrolytic oxidation of perfluoroallylbenzene on a Pt electrode in HSO_3F (with KSO_3F used as a supporting electrolyte), two irreversible waves were recorded; whereas anodic oxidation of perfluoroalk-1-enes under similar conditions was characterized by only one oxidation wave [9]. In addition, preparative electrolytic oxidation of **I** (when the limiting current potentials for the first and the second waves were 1.8 and 2.1 V versus a Cu/Cu^{2+} reference electrode, respectively) gave similar mixtures consisting of the same products, among which α,β-bis(fluorosulfonyloxy)perfluoropropylbenzene **III** was the major product. In addition to **III**, a mixture of high-boiling products was isolated, to which structures polyfluorosulfates **VI–VIII** were assigned on the basis of GC–MS data (Scheme 1).

Such factors as the negligible difference between the two oxidation wave maxima, the controlled potential coulometric data for the first and the second potential ranges of the CV-curve that confirm the two-electron character of oxidation on the both ranges, and primarily the structures of products **III** and **IV** that formed in the course of the electrolysis, indicated that perfluoroallylbenzene (**I**) was not oxidized, but the products of its isomerization (*cis*- and *trans*-perfluoropropenylbenzenes **IV**) and substitutive fluorosulfation (*cis*- and *trans*-3-fluorosulfonyloxyperfluoropropenylbenzenes **V**) (Scheme 1).

Compound **I** in HSO_3F was rapidly converted to a mixture of products whose major components were **IV** and **V** in the ratio of 10:1 (the ratio of *cis*- and *trans*-isomers of **IV** was 1:2.5). Isomerization of perfluoroalk-1-enes to perfluoroalk-2-enes, performed under the action of Lewis acids, is well known [10], however, the similar isomerization using Brönsted acids has not been reported previously.

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E-mail address: grinberg@phyche.ac.ru (V.A. Grinberg).

$$C_6F_5CF_2CF{=}CF_2 \xrightarrow[-HF]{HSO_3F} C_6F_5CF \overset{CF}{\underset{+}{\diagdown\!\!\!\diagup}} CF_2 \longrightarrow$$

$$\xrightarrow{F^-} C_6F_5CF{=}CFCF_3 \quad \text{IV}$$

$$\xrightarrow{FSO_3^-} C_6F_5CF{=}CFCF_2OSO_2F \quad \text{V} \qquad \xrightarrow[\text{anode}]{HSO_3F}$$

$$\longrightarrow C_6F_5(CFOSO_2F)_2CF_3 \;+\; C_6F_5(CFOSO_2F)_2CF_2OSO_2F \;+$$
$$\text{III} \qquad\qquad\qquad \text{VI}$$

$$+\; FSO_3C_6F_6(CFOSO_2F)_2CF_3 \;+\; (FSO_3)_2C_6F_5(CFOSO_2F)_2CF_3$$
$$\text{VII} \qquad\qquad\qquad \text{VIII}$$

Scheme 1.

Thus, the successive transformations that lead to fluorosulfates **III** and **VI–VIII** include both the chemical step of electrophilic isomerization of perfluoroallylbenzene (**I**) with HSO_3F (which is accompanied by substitutive fluorosulfation of **I**) and the electrochemical steps of oxidative fluorosulfation of the olefin double bond of **IV** and **V** and, to a minor extent, of the aromatic ring.

Electrolytic oxidation of perfluoropropenylbenzene **IV** in HSO_3F is the more convenient preparative method for the synthesis of bisfluorosulfate **III**, because in this case the purity of the target product **III** is higher and its yield increases to 78 from 50%.

The main waves on the CV-curve for electrolytic oxidation of perfluoropropenylbenzene isomers (**IV**) coincide in their potentials with the waves of electrolytic oxidation of a perfluoroallylbenzene solution in HSO_3F.

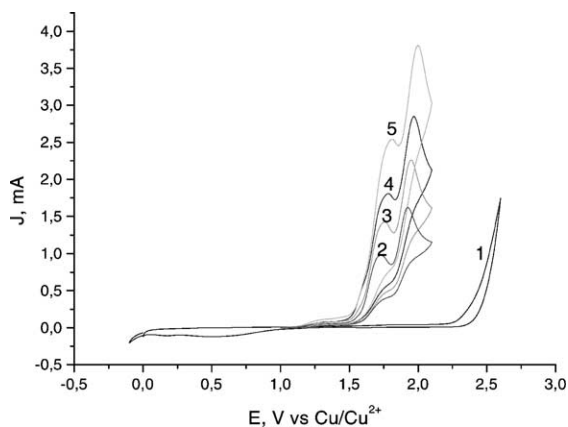Fig. 1 presents CV-curves of isomers **IV** recorded on a Pt electrode in HSO_3F (with KSO_3F used as a supporting

Fig. 1. Cyclic voltammograms for a mixture of HSO_3F and KSO_3F (0.25 M) recorded on a Pt electrode (1); in the presence of $C_6F_5CF{=}CFCF_3$ (7.9×10^{-2} cm^2) at various scan rates (mV/s): (2) 20; (3) 50; (4) 100; (5) 200.

electrolyte) at various potential sweep rates. Electrolytic oxidation of isomers **IV** on a Pt electrode is characterized by two irreversible waves and occurs under "mixed" kinetics conditions. At the point of the CV-curve maximum for the first wave, the plot for the dependence of the reverse rate of oxidation of one of the isomers **IV** upon the reverse square root of potential sweep rate is linear and passes through the origin of coordinates. This dependence is also linear for the second wave and the Y-intercept is equal to 0.1 mA^{-1}. These data indicate that at the point of the CV-curve maximum for the first wave, the rate of electrolytic oxidation for the corresponding isomer of **IV** is limited by its diffusion to the electrode surface and at the point of the maximum of the second wave, electrolytic oxidation of the second isomer is limited both by diffusion to the electrode surface and by electron transfer. In our opinion, this is consistent with its higher oxidation potential.

Therefore, if we compare the values of oxidation current for both isomers (see Fig. 1) with isomer composition of **IV** (that formed as a result of isomerization of **I** under the action of HSO_3F), we assume that the first wave on CV-curve ($E_{max} = 1.8$ V) can be assigned to oxidation of the *cis*-isomer, and the second wave ($E_{max} = 2.1$ V) can be assigned to oxidation of the *trans*-isomer of **IV**.

Unlike fluorinated aliphatic vicinal bisfluorosulfates, which can be easily converted to diperfluoroalkyl-α-diones by reacting with alkali metal fluorides [2], α,β-bis(fluorosulfonyloxy)perfluoropropylbenzene **III** does not react with CsF in the absence of solvent even on heating up to 100 °C. Compound **III** reacted with CsF only in tetraglyme at ca. 80 °C to give perfluoro-2-methyloxolene (**X**), not perfluoromethylphenyl-α-dione **IX**, as was expected. The formation of oxolene **X** can be represented by Scheme 2 whose key step is the generation of oxide **XII** as a result of intramolecular nucleophilic substitution of fluorosulfonyloxy anion in alkoxide **XI**.
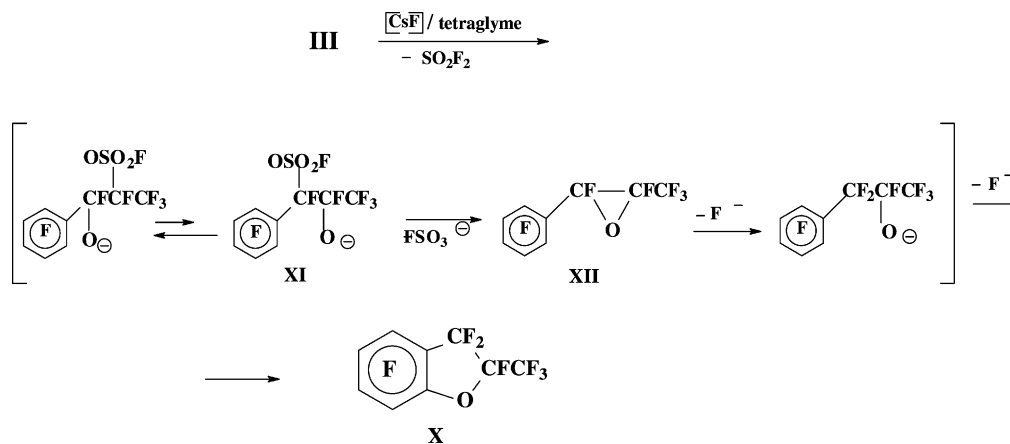
Scheme 2.
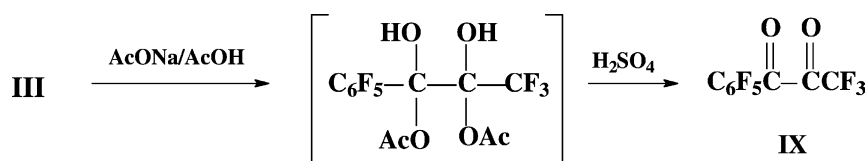
Scheme 3.
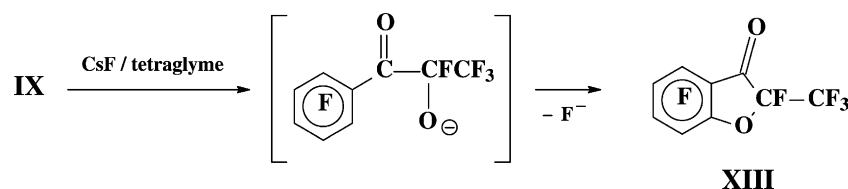
Scheme 4.

The formation of α-oxides and their derivatives in reactions of vicinal bis(fluorosulfonyloxy)perfluoroalkanes with CsF in polar aprotic solvents was reported earlier [11].

Nucleophilic cleavage of perfluorinated polyfluorosulfates in a protic medium suppresses intramolecular nucleophilic substitution of the fluorosulfonyloxy group to make it possible to obtain diperfluoroalkyl-α-polyketones in good yields [12]. Actually, when bisfluorosulfate **III** is treated with sodium acetate in acetic acid, it is converted to perfluoromethylphenyl-α-dione (**IX**) in 70% yield (Scheme 3).

In conclusion, we should note that α-dione also undergoes cyclization in the presence of CsF to give perfluoro-2-methyl-3-oxobenzoxolene (**XIII**) (Scheme 4).

Thus, we can assume that the formation of oxolenes **XII** and **XIII** reflects a trend typical of perfluorinated benzyl ketones, namely, to undergo cyclization under conditions of nucleophilic catalysis.

3. Experimental

The preparative electrolytic syntheses and cyclic voltammetric measurements were carried out with a PAR potentiostat/galvanostat (model 273) with PC monitoring via a GPIB controller.
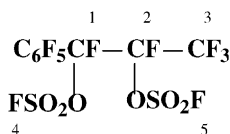
The ^{19}F NMR spectra of the compounds synthesized were recorded on a Bruker WP-200 SY (188 MHz) spectrometer with CF_3CO_2H used as the external standard. The chemical shifts are given in ppm. The mass-spectra were recorded on a VG-7070 GC–MS instrument (70 eV, OV-101, 30 °C, 5 °C/min).

3.1. Electrolytic oxidation of perfluoroallylbenzene (I) in HSO₃F

A mixture of compound **I** (17 g, 57 mmol), HSO_3F (42.5 g), and KSO_3F (1.2 g) was electrolyzed on a Pt anode (8 cm^2) using a steel cathode (1 cm^2) in a one-compartment cell at working potential 2.2 V (against Cu/Cu^{2+} reference electrode) and at 25–28 °C. After 14 kC were passed, the electrolyte was poured into ice, the organic layer was separated, washed with water, extracted with CFC-113 ($CF_2ClCFCl_2$). The resulting extract was dried over MgSO$_4$, distilled under vacuum to give (i) a fraction with bp 60–80 °C/1–1.5 mm (15.3 g) and (ii) a fraction with bp 105–120 °C/1–1.5 mm (3.5 g). Redistillation of the first fraction

gave product **III** (in the form of 2 diastereoisomers, bp 65–67 °C/1 mm, 14.5 g, 52%), current efficiency 40%. Analysis: calc. for $C_9F_{12}O_6S_2$: C, 21.77; F, 45.97; S, 12.90%. Found: C, 22.05; F, 45.74; S, 12.67%. ^{19}F NMR (**III**): −128.0 and −125.7 ($1F^4 + 1F^5$); 1.1 ($3F^3$); 38.4 and 40.5 ($1F^1$); 60.8 (2 *o*-F); 61.5 ($1F^2$); 64.0 (1 *p*-F); 83.5 (2 *m*-F).

$$\underset{\underset{4}{FSO_2O}}{C_6F_5\overset{1}{C}F}-\underset{\underset{5}{OSO_2F}}{\overset{2}{C}F}-\overset{3}{C}F_3$$

Formula of compound III

The second fraction a mixture of trifluorosulfates **VI–VII** and tetrafluorosulfate **VIII** (**VI**:**VII**:**VIII** ≈ 3:1:3) (GC–MS). MS (*m/z*, species, intensity, %) (**VI**): 576 [*M*]$^+$ 20; 297 $[C_7F_7O_3S]^+$ 45; 214 $[C_7F_6O]^+$ 50; 195 $[C_7F_5O]^+$ 100; 186 $[C_6F_6]^+$ 20; 167 $[C_3F_5O]^+$ 10; 149 $[C_3F_5O]^+$ 15; 83 $[C_9F_8O]^+$ 8.

MS (*m/z*, species, intensity, %) (**VII**): 614 [*M*]$^+$ 5; 595 [*M* − F]$^+$?; 515 [*M* − FSO_3]$^+$ 30; 496 $[C_9F_{12}O_6S_2]^+$ 100; 415 $[C_7F_9O_6S_2]^+$ 50; 397 $[C_9F_{11}O_3S]^+$ 30; 347 $[C_8F_9O_3S]^+$ 50; 295 $[C_9F_9O]^+$ 25; 267 $[C_8F_9]^+$ 85; 248 $[C_8F_8]^+$ 75; 217 $[C_7F_7]^+$ 100; 198 $[C_7F_6]^+$ 20; 179 $[C_7F_5]^+$ 35; 167 $[C_6F_5]^+$ 10; 149 $[C_3F_5O]^+$ 65; 117 $[C_5F_3]^+$ 10; 83 $[SO_2F]^+$ 90; 69 $[CF_3]^+$ 35; 47 $[COF]^+$ 70.

MS (*m/z*, species, intensity, %) (**VIII**): 694 [*M*]$^+$ 14; 595 [*M* − FSO_3]$^+$ 52; 495 $[C_7F_9O_9S_3]^+$ 52; 393 $[C_7F_7O_7S_2]^+$ 30; 313 $[C_7F_7O_4S)]^+$ 20; 297 $[C_7F_7O_3S]^+$ 30; 214 $[C_7F_6O]^+$ 20; 195 $[C_7F_5O]^+$ 30; 183 $[C_6F_5O]^+$ 30; 97 $[C_2F_3O]^+$ 25; 83 $[SO_2F]^+$ 100; 69 $[CF_3]^+$ 40; 51 $[CF_2H]^+$ 35.

3.2. Electrolytic oxidation of perfluoropropenylbenzene (IV) in HSO_3F

A mixture of compound **IV** (3 g, 10.1 mmol), HSO_3F (17 g), and KSO_3F (0.5 g) was electrolyzed on a Pt anode (2 cm^2) using a steel cathode (0.5 cm^2) in a one-compartment cell at working potential 2.2 V (versus Cu/Cu^{2+} reference electrode) and at 25–28 °C. After 1995 Coul were passed, the electrolyte was worked up as described in the previous experiment and distillation gave product **III**, bp 64–68 °C/1–1.5 mm (3.5 g); (the starting **IV** (0.3 g) was condensed in a trap). The chemical yield of **III** was 78% on the basis of **IV** that reacted; current efficiency was 89%.

3.3. Reaction of bisfluorosulfate III with CsF

A mixture of compound **III** (3.2 g, 0.065 mol), CsF (1.4 g, 0.092 mol), and tetraglyme (1 ml) was heated to 125 °C with stirring for 1 h. Volatile products (70 °C/1.5–2 mm) were distilled off and collected in a trap (−78 °C); redistillation gave perfluoro-2-methylbenzoxolene **X** (1.85 g, 91%, bp 74–76 °C/70 mm. Found: C, 34.71; F, 59.61. Calculated for $C_9F_{10}O$: C, 34.39; F, 60.51%.
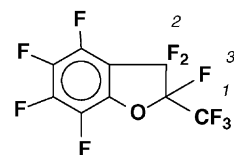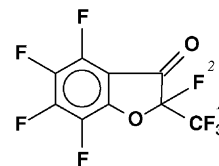

Formula of compound X

^{19}F NMR: 5.3 + 5.35 ($3F^1$); 25.2 + 31.2 (AB-system), J(AB) = 235 Hz ($2F^2$); 57.0 ($1F^3$); 64.5 + 68.7 (2 *o*-F); 83.6 + 84.4 (2 *m*-F).

3.4. Reaction of bis(fluorosulfate) III with AcONa/AcOH

Bisfluorosulfate **III** (13 g, 0.026 mol) was gradually added to a mixture of AcONa (5 g, 0.061 mol) and AcOH (25 ml); the resulting mixture was stirred at 70–80 °C until gas liberation was completed, and poured into water, acidified with 30% H_2SO_4, and extracted with Et_2O. The extract was concentrated, the residue was distilled over H_2SO_4 to collect a fraction with bp 70–90 °C/35 mm (5.8 g). Redistillation gave α-diketone (**IX**) (5.4 g, 70%, bp 76–78 °C/33 mm), which was identified by comparison with an authentic sample [13].

3.5. Reaction of diketone IX with CsF

A mixture of diketone **IX** (4.3 g, 0.0137 mol), CsF (0.7 g), and tetraglyme (2 ml) was heated to 120 °C with stirring. Volatile products with bp up to 70 °C/1.5–2 mm were distilled off and collected in a trap (−78 °C). Redistillation gave perfluoro-2-methyl-3-oxobenzoxolene **VIII** (3.2 g, 75%, bp 170–172 °C). IR(v, cm^{-1}): 1515, 1555, 1575, 1785.

Formula of compound XIII

^{19}F NMR: 6.2 br.d ($3F^1$); 58 br.q ($1F^2$), J(F^1−F^3) = 5.8 Hz; 57.5 + 59.7 (2 *o*-F); 83.6 + 84.2 (2 *m*-F). Found: C, 36.95; F, 52.16. Calculated for $C_9F_8O_2$: C, 36.98; F, 52.05%.

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